PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-068149

(43)Date of publication of application : 16.03.2001

(51)Int.Cl. H01M 10/36
H01M 4/02
H01M 4/58

(21)Application number : 11-244040

(22)Date of filing : 30.08.1999

(71)Applicant : KYOCERA CORP

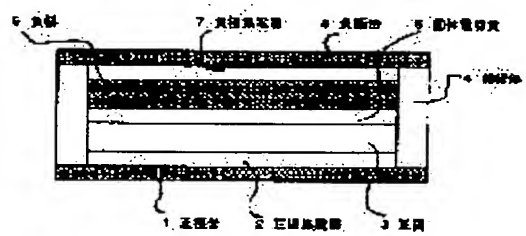
(72)Inventor : HARA TORU
KITAHARA NOBUYUKI
KAMIMURA TOSHIHIKO
MISHIMA HIROMITSU
UMAGOME SHINJI
OSAKI MAKOTO
HIGUCHI HISASHI

(54) ALL SOLID LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To relax remaining stress according to lithium ion diffusion within solid electrolyte particles, eliminate deterioration in internal resistance over a long period of time, and provide a battery with small capacity deterioration.

SOLUTION: A lithium secondary battery assembled by interposing a solid electrolyte 5 between a positive electrode and a negative electrode both made of an active material and sealing them in an outer package has the solid electrolyte made of a sintered body containing a lithium transition metal composite oxide having at least one kind of layer structure of Li_2MnO_3, Li_2TiO_3, and α-$LiAlO_2$.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

CLAIMS

[Claim(s)]
[Claim 1] It sets to the lithium secondary battery which pinched the solid electrolyte between the positive electrodes and negative electrodes which consist of an active material, and was enclosed with it in the sheathing package, and they are Li2 MnO3, Li2 TiO3, or alpha-LiAlO 2 about said solid electrolyte. All solid-state lithium secondary batteries characterized by forming with the sintered compact containing the lithium transition-metals multiple oxide which has at least one kind of rock salt mold layer structure inside.
[Claim 2] In the lithium secondary battery which pinched the solid electrolyte between the positive electrodes and negative electrodes which consist of an active material, and was enclosed with it in the sheathing package It is said positive electrode Lix Mn2-x O4 or (1.05<=X<=1.2) Lix NiY Mn2-X-YO4 of spinel type structure While forming with a sintered compact (1.0<=X<=1.2, 0.4<=Y<0.6) They are Lix Mn2-x O4 of spinel type structure, or (1.25<=X<=1.40) Lix Ti2-x O4 about said negative electrode. All solid-state lithium secondary batteries characterized by forming with a sintered compact (1.25<=X<=1.40).

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] Especially this invention relates to all the solid-state lithium secondary batteries that pinch a solid electrolyte between the positive electrodes and negative electrodes which consist of an active material, and are enclosed with it in a sheathing package about all solid-state lithium secondary batteries.
[0002]
[Description of the Prior Art] There is a remarkable thing in high-performance-izing and a miniaturization of a notebook computer in recent years, a cellular phone, etc. of a portable electronic device, and the cell used for these pocket device requires the much more formation of a high energy consistency and the much more miniaturization.
[0003] As what meets such a demand, the lithium secondary battery using the ejection and insertion of a lithium ion is studied briskly.
[0004] However, since the conventional lithium secondary battery is using nonaqueous electrolyte, it has a problem of the rise of the internal resistance by a liquid spill of the electrolytic solution or deposit of the electrolytic-solution decomposition product in an active material front face.
[0005] In order to solve such a problem, development of all the solid-state lithium secondary batteries that do not use any electrolytic solution is considered.
[0006] JP,6-111831,A -- MnO2 or a lithium compound is reacted to the front face of the positive electrode which consists of an alkali-metal manganese multiple oxide -- making -- Li2 MnO3 of a solid electrolyte Making it generate is advocated. According to this approach, since the adhesion of a positive electrode and a solid electrolyte is good, there is an advantage that interfacial resistance is low.
[0007] However, Li2 MnO3 Since it acts also as an active material which has charge and discharge potential in the 3V neighborhood, the very thing may check the charge-and-discharge reaction of a positive electrode, and the expansion contraction by the ejection and insertion of a lithium ion may also produce destruction of solid-state structure from a certain thing in that case, and, at this rate, it cannot serve as a solid electrolyte which can be used over a long period of time.
[0008] Furthermore, by JP,6-111831,A, when using a solid electrolyte, and an active material carries out expansion contraction at the time of the charge and discharge of an indispensable place, the method of avoiding the danger that the contact in the interface of an electrode and a solid electrolyte will be lost is not stated.
[0009] Moreover, in JP,6-275314,A, while using transition-metals oxide as a positive electrode, the lithium secondary battery which consists of a sulfide system lithium ion conductivity solid electrolyte with the ionic conductivity of bulk higher than an oxide system lithium ion conductivity solid electrolyte as a solid electrolyte is advocated.
[0010] However, since oxygen and the moisture of a minute amount decompose and a sulfide loses the work as a solid electrolyte, it has the fault that it can be hard to obtain a reliable cell.
[0011] This invention is made in view of the trouble of such a conventional technique, a solid

electrolyte and an electrode carry out expansion contraction, and contact of the interface of a solid electrolyte and an electrode is spoiled, and it aims at offering all the solid-state lithium secondary batteries that canceled the conventional trouble that a solid electrolyte decomposed with oxygen and the moisture of a minute amount.

[0012]

[Means for Solving the Problem] It sets to the lithium secondary battery which pinched the solid electrolyte between the positive electrodes and negative electrodes which consist of an active material in all the solid-state lithium secondary batteries concerning claim 1, and was enclosed with it in the sheathing package in order to attain the above-mentioned purpose, and they are Li2 MnO3, Li2 TiO3, or alpha-LiAlO 2 about said solid electrolyte. It is characterized by forming with the sintered compact containing the lithium transition-metals multiple oxide which has at least one kind of rock salt mold layer structure inside.

[0013] moreover, in all the solid-state lithium secondary batteries concerning claim 2 In the lithium secondary battery which pinched the solid electrolyte between the positive electrodes and negative electrodes which consist of an active material, and was enclosed with it in the sheathing package It is said positive electrode Lix Mn2-x O4 or (1.05<=X<=1.2) Lix NiY Mn2-X-Y O4 of spinel type structure While forming with a sintered compact (1.0<=X<=1.2, 0.4<=Y<0.6) They are Lix Mn2-x O4 of spinel type structure, or (1.25<=X<=1.40) Lix Ti2-x O4 about said negative electrode. It is characterized by forming with a sintered compact (1.25<=X<=1.40).

[0014]

[Embodiment of the Invention] Hereafter, the operation gestalt of invention concerning each claim is explained. the sectional view showing the example of a configuration of all the solid-state lithium secondary batteries of invention which drawing 1 requires for claim 1 and claim 2 -- it is -- 1 -- a positive-electrode can and 2 -- for the insulating section and 5, as for a negative electrode and 7, a solid electrolyte and 6 are [a positive-electrode current collection layer and 3 / a positive electrode and 4 / a negative-electrode current collection layer and 8] negative-electrode cans. A sheathing package consists of a positive-electrode can 1, a negative-electrode can 8, and the insulating section 4.

[0015] In a solid electrolyte 5, it is Li2 MnO3. Or Li2 TiO3 Or alpha-LiAlO 2 It uses. This solid electrolyte has the layer structure of a rock salt mold.

[0016] as the raw material which constitutes (1) solid-electrolyte fine particles or a solid electrolyte in order to produce a solid electrolyte 5 -- LiOH, LiOH-H2 O, and Li2 CO3 etc. -- with a lithium compound titanium compounds, such as manganese compounds, such as MnO, MnO2, and MnOOH, or TiO2, or aluminum 2O3 etc. -- with an aluminium compound How to judge and sinter, after distributing the water or the organic solvent in which the shaping assistant was dissolved, adjusting a slurry, carrying out tape forming of this slurry and drying, Or the approach of sintering, after adding a direct or shaping assistant, corning the raw material which constitutes (2) solid electrolytes or a solid electrolyte, supplying to metal mold and carrying out pressing with a press machine etc. is used.

[0017] As an usable shaping assistant, one sort or two sorts or more of mixture, such as polyacrylic acid, a carboxymethyl cellulose, polyvinyl alcohol, diacetyl cellulose, hydroxypropylcellulose, and the poly butyral, is mentioned here, for example.

[0018] The active material which consists of Lix Mn2-x O4 or (1.05<=X<=1.2) Lix NiY Mn2-X-Y O4 of spinel type structure (1.0<=X<=1.2, 0.4<=Y<0.6) is used for a positive electrode 3.

[0019] Here, if the effectiveness of suppressing the expansion contraction at the time of charge and discharge is not enough if X of Lix Mn2-x O4 (1.05<=X<=1.2) is smaller than 1.05, and X is larger than 1.2, since the fall of charge-and-discharge capacity is remarkable, the advantage used for a positive electrode will be spoiled.

[0020] Moreover, although it is the positive-electrode ingredient of high potential, since nickel will not have dissolved and Lix NiY Mn2-X-Y O4 (1.0<=X<=1.2, 0.4<=Y<0.6) will generate an impurity phase if sufficient high potential will not be obtained as compared with Lix Mn2-x O4 (1.05<=X<=1.2) if this Y is smaller than 0.4, and Y becomes 0.6 or more, it is not desirable.

[0021] The active material which consists of Lix Mn2-x O4 of spinel type structure or (1.25<=X<=1.40) Lix Ti2-x O4 (1.25<=X<=1.40) is used for a negative electrode 6. The

effectiveness of suppressing the expansion contraction at the time of charge and discharge if X of Lix Mn2-x O4 or (1.25<=X<=1.40) Lix Ti2-x O4 (1.25<=X<=1.40) is smaller than 1.25 here is not enough, and since a lithium will not have dissolved and an impurity phase will be generated if X is larger than 1.4, it is not desirable.

[0022] The raw material which constitutes (1) active material, a solid electrolyte, or a solid electrolyte in order to produce a positive electrode 3 and a negative electrode 6, Distribute the water or the organic solvent in which the electric conduction agent and the shaping assistant were dissolved, and a slurry is adjusted. How to judge and sinter, after carrying out tape forming of this slurry and drying, Or the approach of sintering, after adding a direct or shaping assistant, corning the raw material which constitutes (2) active materials, a solid electrolyte, or a solid electrolyte, and an electric conduction agent, supplying to metal mold and carrying out pressing with a press machine etc. is used.

[0023] As an usable shaping assistant, one sort or two sorts or more of mixture, such as polyacrylic acid, a carboxymethyl cellulose, polyvinyl alcohol, diacetyl cellulose, hydroxypropylcellulose, and the poly butyral, is mentioned here, for example.

[0024] as the electric conduction agent added by a positive electrode 3 and the negative electrode 6 -- WO3 etc. -- it is.

[0025] The sintering conditions of a solid electrolyte 5, a positive electrode 3, and a negative electrode 6 are suitably chosen from 30 minutes within the limits of 30 hours according to the synthetic conditions of the presentation of an active material or a solid electrolyte, an active material, or a solid electrolyte, or the size of a sintered compact at 500 to 900 degrees C.

[0026] The positive-electrode current collection layer 2 and the negative-electrode current collection layer 7 consist of electroconductive glue which has been arranged for contact to the positive-electrode can 1, a positive electrode 3, or the negative-electrode can 8 and a negative electrode 6, and current collection, for example, contained conductive particles, such as gold, silver, copper, aluminum, nickel, and conductive carbon.

[0027] It is arranged in order that the positive-electrode can 1 and the negative-electrode can 8 may prevent inhibition of the charge-and-discharge reaction by the moisture in atmospheric air, and in order to use as a terminal of a positive electrode 3 and a negative electrode 6, for example, the sheet metal of metals, such as aluminum, copper, nickel, stainless steel, and titanium, is used.

[0028] In order that the insulating section 4 may prevent the internal short circuit of a positive electrode 3 and a negative electrode 6, it is arranged, for example, macromolecules, such as polyethylene, polypropylene, and polyimide, are used.

[0029] A sheathing package consists of a positive-electrode can 1, the insulating section 4, and a negative-electrode can 8.

[0030]

[Example 1] as positive active material -- Li1.1 Mn 1.9O4 as 90wt(s)% and a solid electrolyte -- Li2 MnO3 as a 3wt(s)% and electric conduction agent -- WO3 7wt(s)% -- with the included positive-electrode Plastic solid as a solid electrolyte -- Li2 MnO3 100wt(s)% -- with the included solid electrolyte Plastic solid as a negative-electrode active material -- Li1.33Mn 1.67O4 as 90wt(s)% and a solid electrolyte -- Li2 MnO3 as a 3wt(s)% and electric conduction agent -- WO3 7wt(s)% -- the laminating of the included negative-electrode Plastic solid was carried out, and all solid-state lithium secondary battery components were produced by processing at 750 degrees C for 20 hours.

[0031] As for the size of all the produced solid-state lithium secondary battery components, for the positive electrode, 100 micrometers and a solid electrolyte were [10 micrometers and the negative electrode of phi10mm and thickness] 100 micrometers.

[0032]

[Example 2] as positive active material -- Li1.0 nickel0.5 Mn 1.5O4 as 90wt(s)% and a solid electrolyte -- Li2 MnO3 as a 3wt(s)% and electric conduction agent -- WO3 7wt(s)% -- with the included positive-electrode Plastic solid as a solid electrolyte -- Li2 MnO3 100wt(s)% -- with the included solid electrolyte Plastic solid as a negative-electrode active material -- Li1.33Ti 1.67O4 as 90wt(s)% and a solid electrolyte -- Li2 TiO3 as a 3wt(s)% and electric conduction

agent -- WO_3 7wt(s)% -- the laminating of the included negative-electrode Plastic solid was carried out, and all solid-state lithium secondary battery components were produced by processing at 750 degrees C for 20 hours.
[0033] As for the size of all the produced solid-state lithium secondary battery components, for the positive electrode, 100 micrometers and a solid electrolyte were [10 micrometers and the negative electrode of phi10mm and thickness] 100 micrometers.
[0034] (What has what kind of the layer structure ?)
[0035]
[Example 3] as positive active material -- $Li_{1.1}Mn_{1.9}O_4$ as 90wt(s)% and a solid electrolyte -- Li_2MnO_3 as a 3wt(s)% and electric conduction agent -- WO_3 7wt(s)% -- with the included positive-electrode Plastic solid as a solid electrolyte -- Li_2TiO_3 100wt(s)% -- with the included solid electrolyte Plastic solid as a negative-electrode active material -- $Li_{1.33}Mn_{1.67}O_4$ as 90wt(s)% and a solid electrolyte -- Li_2MnO_3 as a 3wt(s)% and electric conduction agent -- WO_3 7wt(s)% -- the laminating of the included negative-electrode Plastic solid was carried out, and all solid-state lithium secondary battery components were produced by processing at 750 degrees C for 20 hours.
[0036] As for the size of all the produced solid-state lithium secondary battery components, for the positive electrode, 100 micrometers and a solid electrolyte were [10 micrometers and the negative electrode of phi10mm and thickness] 100 micrometers.
[0037]
[Example 4] as positive active material -- $Li_{1.0}$ nickel0.5 $Mn_{1.5}O_4$ as 90wt(s)% and a solid electrolyte -- Li_2MnO_3 as a 3wt(s)% and electric conduction agent -- WO_3 7wt(s)% -- with the included positive-electrode Plastic solid as a solid electrolyte -- gamma-$LiAlO_2$ 100wt(s)% -- with the included solid electrolyte Plastic solid as a negative-electrode active material -- $Li_{1.33}Ti_{1.67}O_4$ as 90wt(s)% and a solid electrolyte -- Li_2TiO_3 as a 3wt(s)% and electric conduction agent -- WO_3 The laminating of the included negative-electrode Plastic solid which was included is carried out. 7wt(s)% -- All solid-state lithium secondary battery components were produced by processing at 750 degrees C for 20 hours.
[0038] As for the size of all the produced solid-state lithium secondary battery components, for the positive electrode, 100 micrometers and a solid electrolyte were [10 micrometers and the negative electrode of phi10mm and thickness] 100 micrometers.
[0039]
[The example 1 of a comparison] as positive active material -- $LiMn_2O_4$ as a 93wt(s)% and electric conduction agent -- WO_3 7wt(s)% -- the front face of the included positive-electrode sintered compact -- LiOH and MnO_2 applying -- the inside of air -- 375 degrees C -- 8 hours -- heat-treating -- Li_2MnO_3 with a thickness of 10 micrometers The solid electrolyte layer was formed. The metal lithium negative electrode was stuck on the solid electrolyte layer, and all solid-state lithium secondary batteries were produced.
[0040] As for the size of all the produced solid-state lithium secondary battery components, for the positive electrode, 100 micrometers and a solid electrolyte were [10 micrometers and the negative electrode of phi10mm and thickness] 100 micrometers.
[0041] The configuration of the forward negative-electrode active material of examples 1-4 and the example 1 of a comparison and a solid electrolyte is collectively shown in Table 1.
[0042] All solid-state lithium secondary batteries were produced because insert in each component into a polyethylene ring with the outer diameter of 12mm, a bore [of 11mm], and a height of 220 micrometers and it pinches and carries out thermocompression bonding to the aluminum sheet metal of two sheets in an argon.
[0043] It is 100microA/cm2 about all the produced solid-state lithium secondary batteries. Charge-and-discharge capacity was measured with current density. The result is shown in Table 2.
[0044]
[Table 1]

試料	正極活物質	負極活物質	固体電解質		
			正極中	中間	負極中
実施例１	４ＶＬＭ	３ＶＬＭ	Ｌ２Ｍ	Ｌ２Ｍ	Ｌ２Ｍ
実施例２	ＬＮＭ	ＬＴ	Ｌ２Ｍ	Ｌ２Ｍ	Ｌ２Ｔ
実施例３	４ＶＬＭ	３ＶＬＭ	Ｌ２Ｍ	Ｌ２Ｔ	Ｌ２Ｍ
実施例４	ＬＮＭ	ＬＴ	Ｌ２Ｍ	ＬＡ	Ｌ２Ｔ
比較例１	ＬＭ'	ＬＭ'	ー　ー　ー	Ｌ２Ｍ	ー　ー　ー

ここで　４ＶＬＭ：$Li_{1.1}Mn_{1.9}O_4$　　３ＶＬＭ：$Li_{1.33}Mn_{1.67}O_4$

ＬＮＭ　：$Li_{1.0}Ni_{0.5}Mn_{1.5}O_4$　　ＬＴ　：$Li_{1.33}Ti_{1.67}O_4$

ＬＭ'　：$LiMn_2O_4$　　Ｌ２Ｍ　：Li_2MnO_3

Ｌ２Ｔ　：Li_2TiO_3　　ＬＡ　：γ－$LiAlO_2$

[0045]
[Table 2]

試料	充放電電圧範囲（Ｖ）	放電容量 (mAh/g) …正極基準	100サイクル後の容量保持率 (%)
実施例１	０．０～２．０	７５	８９．０
実施例２	２．５～４．５	７６	９１．５
実施例３	０．０～２．０	８１	９０．１
実施例４	２．５～４．５	８５	９２．９
比較例１	３．０～４．３	５９	６５．０

[0046] as Table 2 showing -- a solid electrolyte -- Li2 MnO3 Li1.1 Mn 1.9O4 with expansion contraction small to a positive electrode according a sintered compact to charge and discharge Li1.33Mn 1.67O4 with the expansion contraction small to a negative electrode by charge and discharge It is Li2 MnO3 to the used example 1 and a solid electrolyte. A sintered compact Li1.0 nickel0.5 Mn 1.5O4 with the expansion contraction small to a positive electrode by charge and discharge Li1.33Ti 1.67O4 which does not have the expansion contraction by charge and discharge in a negative electrode The used example 2 LiMn 2O4 which is a positive electrode It is solid electrolyte Li2 MnO3 to a sintered compact front face. The capacity retention after 100 cycles improved from the formed example 1 of a comparison.
[0047] Although the example 1 and the example 2 did not have abnormalities in the sample after charge-and-discharge measurement termination, in the example 1 of a comparison, it is weak and the powder considered that the positive electrode and the solid electrolyte were collapsed and generated was also checked.
[0048] Therefore, in the example 1 of a comparison, the expansion contraction at the time of the residual stress accompanying the lithium ion diffusion in the solid electrolyte which is not pressed down and charge and discharge is controlled in an example 1 and the example 2, the contact in the interface of solid electrolyte particles and the interface of an electrode and a solid electrolyte is not lost, but it is surmised that capacity degradation was also suppressed.
[0049] Furthermore, it is Li2 TiO3 as a solid electrolyte to the combination of the same forward negative electrode as an example 1. As for the example 3 using a sintered compact, an example 1 and the effectiveness more than equivalent were seen.
[0050] Furthermore, it is gamma-LiAlO 2 as a solid electrolyte to the combination of the same forward negative electrode as an example 2. As for the example 3 using a sintered compact, an example 2 and the effectiveness more than equivalent were seen.
[0051]
[Effect of the Invention] According to all the solid-state lithium secondary batteries concerning claim 1, a solid electrolyte As mentioned above, Li2 MnO3, Li2 TiO3 or alpha-LiAlO 2 From having formed with the sintered compact containing the lithium transition-metals multiple oxide which has the layer structure of at least one kind of rock salt mold inside A grain boundary will

exist in a solid electrolyte, the residual stress accompanying the lithium ion diffusion in a solid electrolyte particle is eased, and there is no degradation of internal resistance over a long period of time, therefore a cell with little capacity degradation can be offered.
[0052] Moreover, according to all the solid-state lithium secondary batteries concerning claim 2, it is a positive electrode Lix Mn2-x O4 or (1.05<=X<=1.2) Lix NiY Mn2-X-Y O4 of spinel type structure While forming with a sintered compact (1.0<=X<=1.2, 0.4<=Y<0.6) They are Lix Mn2-x O4 of spinel type structure, or (1.25<=X<=1.40) Lix Ti2-x O4 about a negative electrode. From having formed with the sintered compact (1.25<=X<=1.40) Without spoiling contact of the interface of an electrode and a solid electrolyte, since it is small to extent which there is no expansion contraction at the time of the charge and discharge of these active materials, or hardly becomes a problem, there is no degradation of internal resistance over a long period of time, therefore a cell with little capacity degradation can be offered.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention] Especially this invention relates to all the solid-state lithium secondary batteries that pinch a solid electrolyte between the positive electrodes and negative electrodes which consist of an active material, and are enclosed with it in a sheathing package about all solid-state lithium secondary batteries.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] According to all the solid-state lithium secondary batteries concerning claim 1, a solid electrolyte As mentioned above, $Li_2 MnO_3$, $Li_2 TiO_3$ or alpha-$LiAlO_2$ From having formed with the sintered compact containing the lithium transition-metals multiple oxide which has the layer structure of at least one kind of rock salt mold inside A grain boundary will exist in a solid electrolyte, the residual stress accompanying the lithium ion diffusion in a solid electrolyte particle is eased, and there is no degradation of internal resistance over a long period of time, therefore a cell with little capacity degradation can be offered.
[0052] Moreover, according to all the solid-state lithium secondary batteries concerning claim 2, it is a positive electrode $Li_x Mn_{2-x} O_4$ or $(1.05<=X<=1.2)$ $Li_x Ni_Y Mn_{2-X-Y} O_4$ of spinel type structure While forming with a sintered compact $(1.0<=X<=1.2, 0.4<=Y<0.6)$ They are $Li_x Mn_{2-x} O_4$ of spinel type structure, or $(1.25<=X<=1.40)$ $Li_x Ti_{2-x} O_4$ about a negative electrode. From having formed with the sintered compact $(1.25<=X<=1.40)$ Without spoiling contact of the interface of an electrode and a solid electrolyte, since it is small to extent which there is no expansion contraction at the time of the charge and discharge of these active materials, or hardly becomes a problem, there is no degradation of internal resistance over a long period of time, therefore a cell with little capacity degradation can be offered.

[Translation done.]

TECHNICAL PROBLEM

[Description of the Prior Art] There is a remarkable thing in high-performance-izing and a miniaturization of a notebook computer in recent years, a cellular phone, etc. of a portable electronic device, and the cell used for these pocket device requires the much more formation of a high energy consistency and the much more miniaturization.
[0003] As what meets such a demand, the lithium secondary battery using the ejection and insertion of a lithium ion is studied briskly.
[0004] However, since the conventional lithium secondary battery is using nonaqueous electrolyte, it has a problem of the rise of the internal resistance by a liquid spill of the electrolytic solution or deposit of the electrolytic-solution decomposition product in an active material front face.
[0005] In order to solve such a problem, development of all the solid-state lithium secondary batteries that do not use any electrolytic solution is considered.
[0006] JP,6-111831,A -- MnO_2 or a lithium compound is reacted to the front face of the positive electrode which consists of an alkali-metal manganese multiple oxide -- making -- Li_2MnO_3 of a solid electrolyte Making it generate is advocated. According to this approach, since the adhesion of a positive electrode and a solid electrolyte is good, there is an advantage that interfacial resistance is low.
[0007] However, Li_2MnO_3 Since it acts also as an active material which has charge and discharge potential in the 3V neighborhood, the very thing may check the charge-and-discharge reaction of a positive electrode, and the expansion contraction by the ejection and insertion of a lithium ion may also produce destruction of solid-state structure from a certain thing in that case, and, at this rate, it cannot serve as a solid electrolyte which can be used over a long period of time.
[0008] Furthermore, by JP,6-111831,A, when using a solid electrolyte, and an active material carries out expansion contraction at the time of the charge and discharge of an indispensable place, the method of avoiding the danger that the contact in the interface of an electrode and a solid electrolyte will be lost is not stated.
[0009] Moreover, in JP,6-275314,A, while using transition-metals oxide as a positive electrode, the lithium secondary battery which consists of a sulfide system lithium ion conductivity solid electrolyte with the ionic conductivity of bulk higher than an oxide system lithium ion conductivity solid electrolyte as a solid electrolyte is advocated.
[0010] However, since oxygen and the moisture of a minute amount decompose and a sulfide loses the work as a solid electrolyte, it has the fault that it can be hard to obtain a reliable cell.
[0011] This invention is made in view of the trouble of such a conventional technique, a solid electrolyte and an electrode carry out expansion contraction, and contact of the interface of a solid electrolyte and an electrode is spoiled, and it aims at offering all the solid-state lithium secondary batteries that canceled the conventional trouble that a solid electrolyte decomposed with oxygen and the moisture of a minute amount.

[Translation done.]

MEANS

[Means for Solving the Problem] It sets to the lithium secondary battery which pinched the solid electrolyte between the positive electrodes and negative electrodes which consist of an active material in all the solid-state lithium secondary batteries concerning claim 1, and was enclosed with it in the sheathing package in order to attain the above-mentioned purpose, and they are Li2 MnO3, Li2 TiO3, or alpha-LiAlO 2 about said solid electrolyte. It is characterized by forming with the sintered compact containing the lithium transition-metals multiple oxide which has at least one kind of rock salt mold layer structure inside.
[0013] moreover, in all the solid-state lithium secondary batteries concerning claim 2 In the lithium secondary battery which pinched the solid electrolyte between the positive electrodes and negative electrodes which consist of an active material, and was enclosed with it in the sheathing package It is said positive electrode Lix Mn2-x O4 or (1.05<=X<=1.2) Lix NiY Mn2-X-Y O4 of spinel type structure While forming with a sintered compact (1.0<=X<=1.2, 0.4<=Y<0.6) They are Lix Mn2-x O4 of spinel type structure, or (1.25<=X<=1.40) Lix Ti2-x O4 about said negative electrode. It is characterized by forming with a sintered compact (1.25<=X<=1.40).
[0014]
[Embodiment of the Invention] Hereafter, the operation gestalt of invention concerning each claim is explained. the sectional view showing the example of a configuration of all the solid-state lithium secondary batteries of invention which drawing 1 requires for claim 1 and claim 2 -- it is -- 1 -- a positive-electrode can and 2 -- for the insulating section and 5, as for a negative electrode and 7, a solid electrolyte and 6 are [a positive-electrode current collection layer and 3 / a positive electrode and 4 / a negative-electrode current collection layer and 8] negative-electrode cans. A sheathing package consists of a positive-electrode can 1, a negative-electrode can 8, and the insulating section 4.
[0015] In a solid electrolyte 5, it is Li2 MnO3. Or Li2 TiO3 Or alpha-LiAlO 2 It uses. This solid electrolyte has the layer structure of a rock salt mold.
[0016] as the raw material which constitutes (1) solid-electrolyte fine particles or a solid electrolyte in order to produce a solid electrolyte 5 -- LiOH, LiOH-H2 O, and Li2 CO3 etc. -- with a lithium compound titanium compounds, such as manganese compounds, such as MnO, MnO2, and MnOOH, or TiO2, or aluminum 2O3 etc. -- with an aluminium compound How to judge and sinter, after distributing the water or the organic solvent in which the shaping assistant was dissolved, adjusting a slurry, carrying out tape forming of this slurry and drying, Or the approach of sintering, after adding a direct or shaping assistant, corning the raw material which constitutes (2) solid electrolytes or a solid electrolyte, supplying to metal mold and carrying out pressing with a press machine etc. is used.
[0017] As an usable shaping assistant, one sort or two sorts or more of mixture, such as polyacrylic acid, a carboxymethyl cellulose, polyvinyl alcohol, diacetyl cellulose, hydroxypropylcellulose, and the poly butyral, is mentioned here, for example.
[0018] The active material which consists of Lix Mn2-x O4 or (1.05<=X<=1.2) Lix NiY Mn2-X-Y O4 of spinel type structure (1.0<=X<=1.2, 0.4<=Y<0.6) is used for a positive electrode 3.
[0019] Here, if the effectiveness of suppressing the expansion contraction at the time of charge and discharge is not enough if X of Lix Mn2-x O4 (1.05<=X<=1.2) is smaller than 1.05, and X is

larger than 1.2, since the fall of charge-and-discharge capacity is remarkable, the advantage used for a positive electrode will be spoiled.
[0020] Moreover, although it is the positive-electrode ingredient of high potential, since nickel will not have dissolved and Lix NiY Mn2-X-Y O4 (1.0<=X<=1.2, 0.4<=Y<0.6) will generate an impurity phase if sufficient high potential will not be obtained as compared with Lix Mn2-x O4 (1.05<=X<=1.2) if this Y is smaller than 0.4, and Y becomes 0.6 or more, it is not desirable.
[0021] The active material which consists of Lix Mn2-x O4 of spinel type structure or (1.25<=X<=1.40) Lix Ti2-x O4 (1.25<=X<=1.40) is used for a negative electrode 6. The effectiveness of suppressing the expansion contraction at the time of charge and discharge if X of Lix Mn2-x O4 or (1.25<=X<=1.40) Lix Ti2-x O4 (1.25<=X<=1.40) is smaller than 1.25 here is not enough, and since a lithium will not have dissolved and an impurity phase will be generated if X is larger than 1.4, it is not desirable.
[0022] The raw material which constitutes (1) active material, a solid electrolyte, or a solid electrolyte in order to produce a positive electrode 3 and a negative electrode 6, Distribute the water or the organic solvent in which the electric conduction agent and the shaping assistant were dissolved, and a slurry is adjusted. How to judge and sinter, after carrying out tape forming of this slurry and drying, Or the approach of sintering, after adding a direct or shaping assistant, corning the raw material which constitutes (2) active materials, a solid electrolyte, or a solid electrolyte, and an electric conduction agent, supplying to metal mold and carrying out pressing with a press machine etc. is used.
[0023] As an usable shaping assistant, one sort or two sorts or more of mixture, such as polyacrylic acid, a carboxymethyl cellulose, polyvinyl alcohol, diacetyl cellulose, hydroxypropylcellulose, and the poly butyral, is mentioned here, for example.
[0024] as the electric conduction agent added by a positive electrode 3 and the negative electrode 6 -- WO3 etc. -- it is.
[0025] The sintering conditions of a solid electrolyte 5, a positive electrode 3, and a negative electrode 6 are suitably chosen from 30 minutes within the limits of 30 hours according to the synthetic conditions of the presentation of an active material or a solid electrolyte, an active material, or a solid electrolyte, or the size of a sintered compact at 500 to 900 degrees C.
[0026] The positive-electrode current collection layer 2 and the negative-electrode current collection layer 7 consist of electroconductive glue which has been arranged for contact to the positive-electrode can 1, a positive electrode 3, or the negative-electrode can 8 and a negative electrode 6, and current collection, for example, contained conductive particles, such as gold, silver, copper, aluminum, nickel, and conductive carbon.
[0027] It is arranged in order that the positive-electrode can 1 and the negative-electrode can 8 may prevent inhibition of the charge-and-discharge reaction by the moisture in atmospheric air, and in order to use as a terminal of a positive electrode 3 and a negative electrode 6, for example, the sheet metal of metals, such as aluminum, copper, nickel, stainless steel, and titanium, is used.
[0028] In order that the insulating section 4 may prevent the internal short circuit of a positive electrode 3 and a negative electrode 6, it is arranged, for example, macromolecules, such as polyethylene, polypropylene, and polyimide, are used.
[0029] A sheathing package consists of a positive-electrode can 1, the insulating section 4, and a negative-electrode can 8.
[0030]
[Example 1] as positive active material -- Li1.1 Mn 1.9O4 as 90wt(s)% and a solid electrolyte -- Li2 MnO3 as a 3wt(s)% and electric conduction agent -- WO3 7wt(s)% -- with the included positive-electrode Plastic solid as a solid electrolyte -- Li2 MnO3 100wt(s)% -- with the included solid electrolyte Plastic solid as a negative-electrode active material -- Li1.33Mn 1.67O4 as 90wt(s)% and a solid electrolyte -- Li2 MnO3 as a 3wt(s)% and electric conduction agent -- WO3 7wt(s)% -- the laminating of the included negative-electrode Plastic solid was carried out, and all solid-state lithium secondary battery components were produced by processing at 750 degrees C for 20 hours.
[0031] As for the size of all the produced solid-state lithium secondary battery components, for

the positive electrode, 100 micrometers and a solid electrolyte were [10 micrometers and the negative electrode of phi10mm and thickness] 100 micrometers.

[0032]

[Example 2] as positive active material -- Li1.0 nickel0.5 Mn 1.5O4 as 90wt(s)% and a solid electrolyte -- Li2 MnO3 as a 3wt(s)% and electric conduction agent -- WO3 7wt(s)% -- with the included positive-electrode Plastic solid as a solid electrolyte -- Li2 MnO3 100wt(s)% -- with the included solid electrolyte Plastic solid as a negative-electrode active material -- Li1.33Ti 1.67O4 as 90wt(s)% and a solid electrolyte -- Li2 TiO3 as a 3wt(s)% and electric conduction agent -- WO3 7wt(s)% -- the laminating of the included negative-electrode Plastic solid was carried out, and all solid-state lithium secondary battery components were produced by processing at 750 degrees C for 20 hours.

[0033] As for the size of all the produced solid-state lithium secondary battery components, for the positive electrode, 100 micrometers and a solid electrolyte were [10 micrometers and the negative electrode of phi10mm and thickness] 100 micrometers.

[0034] (What has what kind of the layer structure ?)

[0035]

[Example 3] as positive active material -- Li1.1 Mn 1.9O4 as 90wt(s)% and a solid electrolyte -- Li2 MnO3 as a 3wt(s)% and electric conduction agent -- WO3 7wt(s)% -- with the included positive-electrode Plastic solid as a solid electrolyte -- Li2 TiO3 100wt(s)% -- with the included solid electrolyte Plastic solid as a negative-electrode active material -- Li1.33Mn 1.67O4 as 90wt(s)% and a solid electrolyte -- Li2 MnO3 as a 3wt(s)% and electric conduction agent -- WO3 7wt(s)% -- the laminating of the included negative-electrode Plastic solid was carried out, and all solid-state lithium secondary battery components were produced by processing at 750 degrees C for 20 hours.

[0036] As for the size of all the produced solid-state lithium secondary battery components, for the positive electrode, 100 micrometers and a solid electrolyte were [10 micrometers and the negative electrode of phi10mm and thickness] 100 micrometers.

[0037]

[Example 4] as positive active material -- Li1.0 nickel0.5 Mn 1.5O4 as 90wt(s)% and a solid electrolyte -- Li2 MnO3 as a 3wt(s)% and electric conduction agent -- WO3 7wt(s)% -- with the included positive-electrode Plastic solid as a solid electrolyte -- gamma-LiAlO 2 100wt(s)% -- with the included solid electrolyte Plastic solid as a negative-electrode active material -- Li1.33Ti 1.67O4 as 90wt(s)% and a solid electrolyte -- Li2 TiO3 as a 3wt(s)% and electric conduction agent -- WO3 The laminating of the included negative-electrode Plastic solid which was included is carried out. 7wt(s)% -- All solid-state lithium secondary battery components were produced by processing at 750 degrees C for 20 hours.

[0038] As for the size of all the produced solid-state lithium secondary battery components, for the positive electrode, 100 micrometers and a solid electrolyte were [10 micrometers and the negative electrode of phi10mm and thickness] 100 micrometers.

[0039]

[The example 1 of a comparison] as positive active material -- LiMn 2O4 as a 93wt(s)% and electric conduction agent -- WO3 7wt(s)% -- the front face of the included positive-electrode sintered compact -- LiOH and MnO2 applying -- the inside of air -- 375 degrees C -- 8 hours -- heat-treating -- Li2 MnO3 with a thickness of 10 micrometers The solid electrolyte layer was formed. The metal lithium negative electrode was stuck on the solid electrolyte layer, and all solid-state lithium secondary batteries were produced.

[0040] As for the size of all the produced solid-state lithium secondary battery components, for the positive electrode, 100 micrometers and a solid electrolyte were [10 micrometers and the negative electrode of phi10mm and thickness] 100 micrometers.

[0041] The configuration of the forward negative-electrode active material of examples 1-4 and the example 1 of a comparison and a solid electrolyte is collectively shown in Table 1.

[0042] All solid-state lithium secondary batteries were produced because insert in each component into a polyethylene ring with the outer diameter of 12mm, a bore [of 11mm], and a height of 220 micrometers and it pinches and carries out thermocompression bonding to the

aluminum sheet metal of two sheets in an argon.
[0043] It is 100microA/cm2 about all the produced solid-state lithium secondary batteries. Charge-and-discharge capacity was measured with current density. The result is shown in Table 2.
[0044]
[Table 1]

試料	正極活物質	負極活物質	固体電解質		
			正極中	中間	負極中
実施例1	4VLM	3VLM	L2M	L2M	L2M
実施例2	LNM	LT	L2M	L2M	L2T
実施例3	4VLM	3VLM	L2M	L2T	L2M
実施例4	LNM	LT	L2M	LA	L2T
比較例1	LM'	LM'	— — —	L2M	— — —

ここで 4VLM：$Li_{1.1}Mn_{1.9}O_4$ 3VLM：$Li_{1.33}Mn_{1.67}O_4$
LNM ：$Li_{1.0}Ni_{0.5}Mn_{1.5}O_4$ LT ：$Li_{1.33}Ti_{1.67}O_4$
LM' ：$LiMn_2O_4$ L2M ：Li_2MnO_3
L2T ：Li_2TiO_3 LA ：γ－$LiAlO_2$

[0045]
[Table 2]

試料	充放電電圧範囲（V）	放電容量 (mAh/g) …正極基準	100サイクル後の容量保持率 (%)
実施例1	0.0～2.0	75	89.0
実施例2	2.5～4.5	76	91.5
実施例3	0.0～2.0	81	90.1
実施例4	2.5～4.5	85	92.9
比較例1	3.0～4.3	69	65.0

[0046] as Table 2 showing -- a solid electrolyte -- Li2 MnO3 Li1.1 Mn 1.9O4 with expansion contraction small to a positive electrode according a sintered compact to charge and discharge Li1.33Mn 1.67O4 with the expansion contraction small to a negative electrode by charge and discharge It is Li2 MnO3 to the used example 1 and a solid electrolyte. A sintered compact Li1.0 nickel0.5 Mn 1.5O4 with the expansion contraction small to a positive electrode by charge and discharge Li1.33Ti 1.67O4 which does not have the expansion contraction by charge and discharge in a negative electrode The used example 2 LiMn 2O4 which is a positive electrode It is solid electrolyte Li2 MnO3 to a sintered compact front face. The capacity retention after 100 cycles improved from the formed example 1 of a comparison.
[0047] Although the example 1 and the example 2 did not have abnormalities in the sample after charge-and-discharge measurement termination, in the example 1 of a comparison, it is weak and the powder considered that the positive electrode and the solid electrolyte were collapsed and generated was also checked.
[0048] Therefore, in the example 1 of a comparison, the expansion contraction at the time of the residual stress accompanying the lithium ion diffusion in the solid electrolyte which is not pressed down and charge and discharge is controlled in an example 1 and the example 2, the contact in the interface of solid electrolyte particles and the interface of an electrode and a solid electrolyte is not lost, but it is surmised that capacity degradation was also suppressed.
[0049] Furthermore, it is Li2 TiO3 as a solid electrolyte to the combination of the same forward negative electrode as an example 1. As for the example 3 using a sintered compact, an example 1 and the effectiveness more than equivalent were seen.
[0050] Furthermore, it is gamma-LiAlO 2 as a solid electrolyte to the combination of the same forward negative electrode as an example 2. As for the example 3 using a sintered compact, an

example 2 and the effectiveness more than equivalent were seen.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the sectional view showing the example of a configuration of the coin type all solid-state lithium secondary battery in this invention.
[Description of Notations]
1 [.. The insulating section (sheathing package), 5 / .. A solid electrolyte, 6 / .. A negative electrode, 7 / .. A negative-electrode current collection layer, 8 / .. Negative-electrode can (sheathing package)] .... A positive-electrode can (sheathing package), 2 .. A positive-electrode current collection layer, 3 .. A positive electrode, 4

[Translation done.]

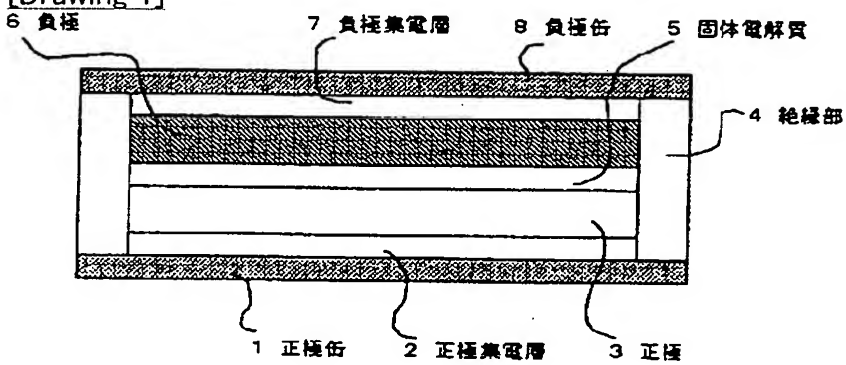
* NOTICES *

JPO and INPIT are not responsible for any
damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Translation done.]

(19)日本国特許庁（ＪＰ）　(12) **公開特許公報**（Ａ）

(11)特許出願公開番号
特開2001－68149
(P2001－68149A)

(43)公開日　平成13年３月16日(2001.3.16)

(51)Int.Cl.⁷	識別記号	ＦＩ	テーマコード（参考）
Ｈ０１Ｍ　10/36		Ｈ０１Ｍ　10/36	Ａ　５Ｈ００３
4/02		4/02	Ａ　５Ｈ０１４
4/58		4/58	５Ｈ０２９

審査請求　未請求　請求項の数２　ＯＬ　（全６頁）

(21)出願番号　特願平11－244040

(22)出願日　平成11年８月30日(1999.8.30)

(71)出願人　000006633
京セラ株式会社
京都府京都市伏見区竹田鳥羽殿町６番地

(72)発明者　原　亨
京都府相楽郡精華町光台３丁目５番地　京セラ株式会社中央研究所内

(72)発明者　北原　暢之
京都府相楽郡精華町光台３丁目５番地　京セラ株式会社中央研究所内

(72)発明者　上村　俊彦
京都府相楽郡精華町光台３丁目５番地　京セラ株式会社中央研究所内

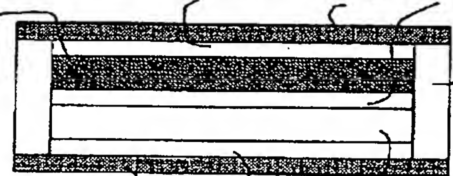
最終頁に続く

(54)【発明の名称】　全固体リチウム二次電池

(57)【要約】

【課題】　固体電解質や電極が膨脹収縮して固体電解質と電極との界面の接触が損なわれ、また固体電解質が微量の酸素や水分によって分解するという問題があった。

【解決手段】　活物質から成る正極と負極との間に固体電解質を挟持して外装パッケージ内に封入したリチウム二次電池において、前記固体電解質をLi_2MnO_3、Li_2TiO_3、または$\alpha-LiAlO_2$のうち少なくとも１種類の層状構造を有するリチウム遷移金属複合酸化物を含む焼結体で形成したことを特徴とする。



1

【特許請求の範囲】

【請求項１】　活物質から成る正極と負極との間に固体電解質を挟持して外装パッケージ内に封入したリチウム二次電池において、前記固体電解質をLi_2MnO_3、Li_2TiO_3、または$\alpha-LiAlO_2$のうち少なくとも１種類の岩塩型層状構造を有するリチウム遷移金属複合酸化物を含む焼結体で形成したことを特徴とする全固体リチウム二次電池。

【請求項２】　活物質から成る正極と負極との間に固体電解質を挟持して外装パッケージ内に封入したリチウム二次電池において、前記正極をスピネル型構造の$Li_xMn_{2-x}O_4$（$1.05 \leqq X \leqq 1.2$）または$Li_xNi_YMn_{2-X-Y}O_4$（$1.0 \leqq X \leqq 1.2$、$0.4 \leqq Y < 0.6$）焼結体で形成するとともに、前記負極をスピネル型構造の$Li_xMn_{2-x}O_4$（$1.25 \leqq X \leqq 1.40$）または$Li_xTi_{2-x}O_4$（$1.25 \leqq X \leqq 1.40$）焼結体で形成したことを特徴とする全固体リチウム二次電池。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は全固体リチウム二次電池に関し、特に活物質から成る正極と負極との間に固体電解質を挟持して外装パッケージ内に封入する全固体リチウム二次電池に関する。

【０００２】

【従来の技術および発明が解決しようとする課題】近年のノートパソコンや携帯電話等の携帯用電子機器の高性能化と小型化にはめざましいものがあり、これら携帯機器に使用される電池では、より一層の高エネルギー密度化と小型化が要求されている。

【０００３】このような要求に応えるものとして、リチウムイオンの脱挿入を利用したリチウム二次電池が盛んに研究されている。

【０００４】しかしながら、従来のリチウム二次電池は非水電解液を使用していることから、電解液の漏液、あるいは活物質表面における電解液分解生成物の析出による内部抵抗の上昇といった問題がある。

【０００５】このような問題を解決するために、電解液を一切使わない全固体リチウム二次電池の開発が検討されている。

【０００６】例えば特開平６－１１１８３１号公報では、MnO_2またはアルカリ金属マンガン複合酸化物からなる正極の表面に、リチウム化合物を反応させて固体電解質のLi_2MnO_3を生成させることが提唱されている。この方法によれば、正極と固体電解質の密着性が良いため、界面抵抗が低いという利点がある。

【０００７】しかしながら、Li_2MnO_3自体は３Ｖ付近に充放電電位を有する活物質としても作用することから、正極の充放電反応を阻害する可能性があり、またその際にリチウムイオンの脱挿入による膨張収縮もあることから、固体構造の破壊を生じる可能性があり、このままでは長期にわたって使用できる固体電解質とはなり得ない。

2

【０００８】さらに、特開平６－１１１８３１号公報では、固体電解質を用いる場合には必須であるところの、充放電時に活物質が膨張収縮することによって電極と固体電解質との界面における接触が失われる危険性を回避する方法については述べられていない。

【０００９】また、特開平６－２７５３１４号公報では、正極として遷移金属酸化物を用いるとともに、固体電解質として酸化物系リチウムイオン伝導性固体電解質よりもバルクのイオン伝導度が高い硫化物系リチウムイオン伝導性固体電解質とからなるリチウム二次電池が提唱されている。

【００１０】しかしながら、硫化物は微量の酸素や水分により分解して固体電解質としての働きを失うため、信頼性の高い電池を得られにくいという欠点がある。

【００１１】本発明はこのような従来技術の問題点に鑑みてなされたものであり、固体電解質や電極が膨張収縮して固体電解質と電極との界面の接触が損なわれ、また固体電解質が微量の酸素や水分によって分解するという従来の問題点を解消した全固体リチウム二次電池を提供することを目的とする。

【００１２】

【課題を解決するための手段】上記目的を達成するために、請求項１に係る全固体リチウム二次電池では、活物質から成る正極と負極との間に固体電解質を挟持して外装パッケージ内に封入したリチウム二次電池において、前記固体電解質をLi_2MnO_3、Li_2TiO_3、または$\alpha-LiAlO_2$のうち少なくとも１種類の岩塩型層状構造を有するリチウム遷移金属複合酸化物を含む焼結体で形成したことを特徴とする。

【００１３】また、請求項２に係る全固体リチウム二次電池では、活物質から成る正極と負極との間に固体電解質を挟持して外装パッケージ内に封入したリチウム二次電池において、前記正極をスピネル型構造の$Li_xMn_{2-x}O_4$（$1.05 \leqq X \leqq 1.2$）または$Li_xNi_YMn_{2-X-Y}O_4$（$1.0 \leqq X \leqq 1.2$、$0.4 \leqq Y < 0.6$）焼結体で形成するとともに、前記負極をスピネル型構造の$Li_xMn_{2-x}O_4$（$1.25 \leqq X \leqq 1.40$）または$Li_xTi_{2-x}O_4$（$1.25 \leqq X \leqq 1.40$）焼結体で形成したことを特徴とする。

【００１４】

【発明の実施の形態】以下、各請求項に係る発明の実施形態を説明する。図１は請求項１および請求項２に係る発明の全固体リチウム二次電池の構成例を示す断面図であり、１は正極缶、２は正極集電層、３は正極、４は絶縁部、５は固体電解質、６は負極、７は負極集電層、８は負極缶である。正極缶１と負極缶８と絶縁部４とで外装パッケージが構成される。

【００１５】固体電解質５には、Li_2MnO_3 または Li_2TiO_3 または$\alpha-LiAlO_2$ を用いる。この固体電解質は岩塩型の層状構造を有する。

【００１６】固体電解質５を作製するには、（１）固体電解質粉体、または固体電解質を構成する原料として$LiOH$、$LiOH\cdot H_2O$、Li_2CO_3 などのリチウム化合物と、MnO、MnO_2 、$MnOOH$などのマンガン化合物、またはTiO_2などのチタン化合物、またはAl_2O_3 などのアルミニウム化合物と、成形助剤とを溶解させた水または有機溶剤に分散させてスラリーを調整し、このスラリーをテープ成形して乾燥した後に裁断して焼結する方法、あるいは、（２）固体電解質または固体電解質を構成する原料を直接あるいは成形助剤を加えて造粒して金型に投入してプレス機で加圧成形した後に焼結する方法などが用いられる。

【００１７】ここで使用可能な成形助剤としては、例えばポリアクリル酸、カルボキシメチルセルロース、ポリビニルアルコール、ジアセチルセルロース、ヒドロキシプロピルセルロース、ポリブチラールなどの１種もしくは２種以上の混合物が挙げられる。

【００１８】正極３には、スピネル型構造の$Li_XMn_{2-X}O_4$（１．０５≦Ｘ≦１．２）または$Li_XNi_YMn_{2-X-Y}O_4$（１．０≦Ｘ≦１．２、０．４≦Ｙ＜０．６）から成る活物質を用いる。

【００１９】ここで、$Li_XMn_{2-X}O_4$（１．０５≦Ｘ≦１．２）のＸが１．０５より小さいと充放電時の膨脹収縮を抑える効果が十分でなく、またＸが１．２より大きいと充放電容量の低下が顕著であるため、正極に用いる利点が損なわれる。

【００２０】また、$Li_XNi_YMn_{2-X-Y}O_4$（１．０≦Ｘ≦１．２、０．４≦Ｙ＜０．６）はより高電位の正極材料であるが、このＹが０．４より小さいと$Li_XMn_{2-X}O_4$（１．０５≦Ｘ≦１．２）に比較して十分な高電位が得られず、またＹが０．６以上になるとＮｉが固溶しきらず、不純物相を生成するので好ましくない。

【００２１】負極６には、スピネル型構造の$Li_XMn_{2-X}O_4$（１．２５≦Ｘ≦１．４０）または$Li_XTi_{2-X}O_4$（１．２５≦Ｘ≦１．４０）から成る活物質を用いる。ここで$Li_XMn_{2-X}O_4$（１．２５≦Ｘ≦１．４０）または$Li_XTi_{2-X}O_4$（１．２５≦Ｘ≦１．４０）のＸが１．２５より小さいと、充放電時の膨張収縮を抑える効果が充分でなく、またＸが１．４より大きいとリチウムが固溶しきらず、不純物相を生成するので好ましくない。

【００２２】正極３および負極６を作製するには、（１）活物質、固体電解質または固体電解質を構成する原料、導電剤、および成形助剤とを溶解させた水または有機溶剤に分散させてスラリーを調整し、このスラリーをテープ成形して乾燥した後に裁断して焼結する方法、あるいは（２）活物質、固体電解質または固体電解質を構成する原料、および導電剤とを直接あるいは成形助剤を加えて造粒して金型に投入してプレス機で加圧成形した後に焼結する方法などが用いられる。

【００２３】ここで使用可能な成形助剤としては、例えばポリアクリル酸、カルボキシメチルセルロース、ポリビニルアルコール、ジアセチルセルロース、ヒドロキシプロピルセルロース、ポリブチラールなどの１種もしくは２種以上の混合物が挙げられる。

【００２４】正極３および負極６に添加される導電剤としてはWO_2 などがある。

【００２５】固体電解質５、正極３、および負極６の焼結条件は、５００℃から９００℃で３０分から３０時間の範囲内で、活物質または固体電解質の組成、活物質または固体電解質の合成条件、あるいは焼結体のサイズに応じて適宜選択される。

【００２６】正極集電層２および負極集電層７は、正極缶１と正極３、あるいは負極缶８と負極６との接触と集電のために配置され、例えば金、銀、銅、アルミニウム、ニッケル、導電性カーボンなどの導電性粒子を含んだ導電性接着剤からなる。

【００２７】正極缶１および負極缶８は、大気中の水分による充放電反応の阻害を防ぐため、および正極３と負極６の端子として用いるために配置され、例えばアルミニウム、銅、ニッケル、ステンレススチール、チタンなどの金属の薄板が用いられる。

【００２８】絶縁部４は、正極３と負極６との内部短絡を防ぐために配置され、例えばポリエチレン、ポリプロピレン、ポリイミドなどの高分子が用いられる。

【００２９】正極缶１、絶縁部４、および負極缶８とで外装パッケージが構成される。

【００３０】

【実施例１】正極活物質として$Li_{1.1}Mn_{1.9}O_4$を９０ｗｔ％、固体電解質としてLi_2MnO_3 を３ｗｔ％、導電剤としてWO_3 を７ｗｔ％含んだ正極成形体と、固体電解質としてLi_2MnO_3 を１００ｗｔ％含んだ固体電解質成形体と、負極活物質として$Li_{1.33}Mn_{1.67}O_4$を９０ｗｔ％、固体電解質としてLi_2MnO_3 を３ｗｔ％、導電剤としてWO_3 を７ｗｔ％含んだ負極成形体を積層して、７５０℃で２０時間処理することにより全固体リチウム二次電池素子を作製した。

【００３１】作製した全固体リチウム二次電池素子のサイズはφ１０ｍｍ、厚さは正極が１００μｍ、固体電解質が１０μｍ、負極が１００μｍであった。

【００３２】

【実施例２】正極活物質として$Li_{1.0}Ni_{0.5}Mn_{1.5}O_4$を９０ｗｔ％、固体電解質として$Li_2MnO_3$ を３ｗｔ％、導電剤としてWO_3 を７ｗｔ％含んだ正極成形体と、固体電解質としてLi_2MnO_3 を１００ｗｔ％含んだ固体電解質成形体と、負極活物質としてＬ

$i_{1.33}$ $Ti_{1.67}$ O_4 を９０ｗｔ％、固体電解質としてＬi_2 TiO_3 を３ｗｔ％、導電剤としてWO_3 を７ｗｔ％含んだ負極成形体を積層して、７５０℃で２０時間処理することにより全固体リチウム二次電池素子を作製した。

【００３３】作製した全固体リチウム二次電池素子のサイズはφ１０mm、厚さは正極が１００μｍ、固体電解質が１０μｍ、負極が１００μｍであった。

【００３４】（何がどのような層状構造になっている？）

【００３５】

【実施例３】正極活物質として$Li_{1.1}$ $Mn_{1.9}$ O_4 を９０ｗｔ％、固体電解質としてLi_2MnO_3 を３ｗｔ％、導電剤としてWO_2 を７ｗｔ％含んだ正極成形体と、固体電解質としてLi_2 TiO_3 を１００ｗｔ％含んだ固体電解質成形体と、負極活物質として$Li_{1.33}$ $Mn_{1.67}$ O_4 を９０ｗｔ％、固体電解質としてLi_2MnO_3 を３ｗｔ％、導電剤としてWO_3 を７ｗｔ％含んだ負極成形体を積層して、７５０℃で２０時間処理することにより全固体リチウム二次電池素子を作製した。

【００３６】作製した全固体リチウム二次電池素子のサイズはφ１０mm、厚さは正極が１００μｍ、固体電解質が１０μｍ、負極が１００μｍであった。

【００３７】

【実施例４】正極活物質として$Li_{1.6}$ $Ni_{0.5}$ $Mn_{1.5}$ O_4 を９０ｗｔ％、固体電解質としてLi_2MnO_3 を３ｗｔ％、導電剤としてWO_3 を７ｗｔ％含んだ正極成形体と、固体電解質としてγ－$LiAlO_2$ を１００ｗｔ％含んだ固体電解質成形体と、負極活物質として$Li_{1.33}$ $Ti_{1.67}$ O_4 を９０ｗｔ％、固体電解質として＊Li_2 TiO_3 を３ｗｔ％、導電剤としてWO_3 を７ｗｔ％含んだ含んだ負極成形体を積層して、７５０℃で２０時間処理することにより全固体リチウム二次電池素子を作製した。

【００３８】作製した全固体リチウム二次電池素子のサイズはφ１０mm、厚さは正極が１００μｍ、固体電解質が１０μｍ、負極が１００μｍであった。

【００３９】

【比較例１】正極活物質として$LiMn_2$ O_4 を９３ｗｔ％、導電剤としてWO_3 を７ｗｔ％含んだ正極焼結体の表面にＬｉＯＨとMnO_2 を塗布し、空気中にて３７５℃で８時間熱処理して、厚さ１０μｍのLi_2MnO_3 固体電解質層を形成した。固体電解質層の上に金属リチウム負極を貼りつけて、全固体リチウム二次電池を作製した。

【００４０】作製した全固体リチウム二次電池素子のサイズはφ１０mm、厚さは正極が１００μｍ、固体電解質が１０μｍ、負極が１００μｍであった。

【００４１】実施例１～４、比較例１の正負極活物質、固体電解質の構成について表１にまとめて示す。

【００４２】各々の素子をアルゴン中にて、外径１２mm、内径１１mm、高さ２２０μｍのポリエチレンリング中にはめ込み、二枚のアルミニウム薄板に挟んで熱圧着することで全固体リチウム二次電池を作製した。

【００４３】作製した全固体リチウム二次電池について１００μＡ／ｃｍ^2 の電流密度で充放電容量を測定した。その結果を表２に示す。

【００４４】

【表１】

試料	正極活物質	負極活物質	固体電解質		
			正極中	中間	負極中
実施例１	４ＶＬＭ	３ＶＬＭ	Ｌ２Ｍ	Ｌ２Ｍ	Ｌ２Ｍ
実施例２	ＬＮＭ	ＬＴ	Ｌ２Ｍ	Ｌ２Ｍ	Ｌ２Ｔ
実施例３	４ＶＬＭ	３ＶＬＭ	Ｌ２Ｍ	Ｌ２Ｔ	Ｌ２Ｍ
実施例４	ＬＮＭ	ＬＴ	Ｌ２Ｍ	ＬＡ	Ｌ２Ｔ
比較例１	ＬＭ’	ＬＭ’	－ － －	Ｌ２Ｍ	－ － －

ここで　４ＶＬＭ：$Li_{1.1}Mn_{1.9}O_4$　　３ＶＬＭ：$Li_{1.33}Mn_{1.67}O_4$

ＬＮＭ　：$Li_{1.0}Ni_{0.5}Mn_{1.5}O_4$　　ＬＴ　：$Li_{1.33}Ti_{1.67}O_4$

ＬＭ’　：$LiMn_2O_4$　　Ｌ２Ｍ　：Li_2MnO_3

Ｌ２Ｔ　：Li_2TiO_3　　ＬＡ　：γ－$LiAlO_2$

【００４５】

【表２】

試料	充放電電圧範囲（V）	放電容量 (mAh/g) …正極基準	100サイクル後の容量保持率 (%)
実施例１	０．０～２．０	７５	８９．０
実施例２	２．５～４．５	７６	９１．５
実施例３	０．０～２．０	８１	９０．１
実施例４	２．５～４．５	８５	９２．９
比較例１	３．０～４．３	６９	６５．０

【００４６】表２からわかる通り、固体電解質にLi_2MnO_3焼結体を、正極に充放電による膨張収縮の小さい$Li_{1.1}Mn_{1.9}O_4$を、負極に充放電による膨張収縮の小さい$Li_{1.33}Mn_{1.67}O_4$を用いた実施例１、および固体電解質にLi_2MnO_3焼結体を、正極に充放電による膨張収縮の小さい$Li_{1.0}Ni_{0.5}Mn_{1.5}O_4$を、負極に充放電による膨張収縮のない$Li_{1.33}Ti_{1.67}O_4$を用いた実施例２は、正極である$LiMn_2O_4$焼結体表面に固体電解質$Li_2MnO_3$を形成した比較例１より１００サイクル後の容量保持率が向上した。

【００４７】実施例１および実施例２は充放電測定終了後のサンプルに異常はなかったが、比較例１では脆くなっており、正極および固体電解質が崩れて発生したと思われる粉も確認された。

【００４８】したがって、比較例１では抑えられていない固体電解質中のリチウムイオン拡散に伴う残留応力と充放電時の膨張収縮が、実施例１および実施例２では抑制され、そのため固体電解質粒子同士の界面および電極と固体電解質との界面における接触が失われず、容量劣化も抑えられたと推測される。

【００４９】さらに、実施例１と同じ正負極の組み合わせに、固体電解質としてLi_2TiO_3焼結体を用いた実施例３は、実施例１と同等以上の効果が見られた。

【００５０】さらに、実施例２と同じ正負極の組み合わせに、固体電解質としてγ－$LiAlO_2$焼結体を用いた実施例３は、実施例２と同等以上の効果が見られた。

【００５１】

【発明の効果】以上のように、請求項１に係る全固体リチウム二次電池によれば、固体電解質をLi_2MnO_3、Li_2TiO_3、またはα－$LiAlO_2$のうち少なくとも１種類の岩塩型の層状構造を有するリチウム遷移金属複合酸化物を含む焼結体で形成したことから、固体電解質中に粒界が存在することになり、固体電解質粒子中のリチウムイオン拡散に伴う残留応力が緩和され、長期にわたって内部抵抗の劣化が無く、したがって容量劣化の少ない電池を提供することができる。

【００５２】また、請求項２に係る全固体リチウム二次電池によれば、正極をスピネル型構造の$Li_XMn_{2-X}O_4$（１．０５≦X≦１．２）または$Li_XNi_YMn_{2-X-Y}O_4$（１．０≦X≦１．２、０．４≦Y＜０．６）焼結体で形成するとともに、負極をスピネル型構造の$Li_XMn_{2-X}O_4$（１．２５≦X≦１．４０）または$Li_XTi_{2-X}O_4$（１．２５≦X≦１．４０）焼結体で形成したことから、これら活物質の充放電時の膨張収縮が全くないかあるいはほとんど問題にならない程度に小さいため、電極と固体電解質との界面の接触が損なわれることなく、長期にわたって内部抵抗の劣化が無く、したがって容量劣化の少ない電池を提供することができる。

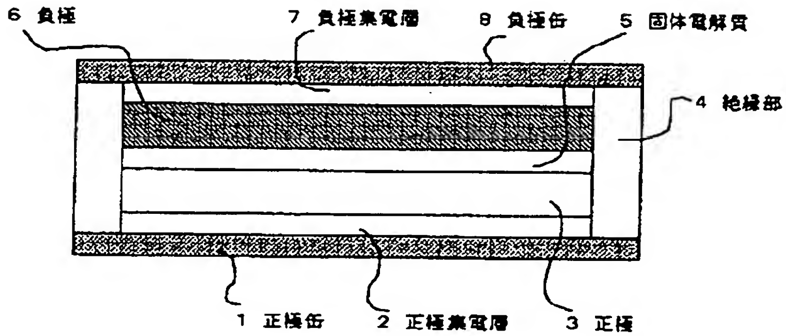
【図面の簡単な説明】

【図１】本発明におけるコイン型全固体リチウム二次電池の構成例を示す断面図である。

【符号の説明】

１……正極缶（外装パッケージ）、２……正極集電層、３……正極、４……絶縁部（外装パッケージ）、５……固体電解質、６……負極、７……負極集電層、８……負極缶（外装パッケージ）

【図１】



【手続補正書】
【提出日】平成１１年９月３日（１９９９．９．３）
【手続補正１】
【補正対象書類名】明細書
【補正対象項目名】００３４
【補正方法】削除

フロントページの続き

(72)発明者　三島　洋光
京都府相楽郡精華町光台３丁目５番地　京セラ株式会社中央研究所内
(72)発明者　馬込　伸二
京都府相楽郡精華町光台３丁目５番地　京セラ株式会社中央研究所内
(72)発明者　大崎　誠
京都府相楽郡精華町光台３丁目５番地　京セラ株式会社中央研究所内
(72)発明者　樋口　永
京都府相楽郡精華町光台３丁目５番地　京セラ株式会社中央研究所内

Ｆターム(参考)　5H003 AA00 BB05 BC05 BC06 BD00
5H014 AA01 AA06 EE10 HH00
5H029 AJ00 AJ14 AK03 AL03 AM12
BJ03 BJ04 DJ17 HJ02 HJ13